

Preparation and Thermoelectric Properties of p- and n-type IrSb₃

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Abstract. IrSb₃ belongs to a large family of compounds with the skutterudite crystal structure (CoAs₃). The peritectic decomposition temperature of IrSb₃ is 1141 °C [1]. The growth of large crystals of IrSb₃ by conventional growth techniques is not straightforward. Single phase, polycrystalline samples were prepared by a liquid-solidsintering technique. Samples were characterized by microprobe analysis, X-ray diffractometry and density measurements. As-prepared IrSb₃ samples show p-type conductivity and n-type samples were prepared by addition of platinum. Seebeck coefficient, electrical resistivity, thermal conductivity and hall effect measurements were performed at room temperature and up to 600°C on selected samples. High p-type mobilities were measured and a maximum of about 1380 cm².V⁻¹.s⁻¹ was measured on a sample with a carrier concentration of 7.1 x 10¹⁸ cm⁻³. N-type samples have substantially lower mobilities but very large Seebeck coefficients. A bandgap of 1.18 eV was estimated from high temperature electrical resistivity and Hall effect measurements. The hole and electron effective masses were also estimated. Based on the experimental data obtained, the potential of IrSb₃ as a thermoelectric material is discussed.

INTRODUCTION

IrSb₃ belongs to a large family of materials having the skutterudite structure and recent studies have shown that it is a promising thermoelectric material [2,3]. This structure is composed of a cubic lattice, space group *Im*3 and the unit cell contains 8 AB₃ groups. The lattice constant of IrSb₃ is 9.2533 Å and its peritectic decomposition temperature is 1141 °C [1]. The growth of large crystals of IrSb₃ by conventional growth techniques is not straightforward because crystal growth from the melt can only be initiated from a very narrow range of compositions [1]. Moreover, the liquidus curve in this region is so sharp that the separation of the liquid and the solid during crystallization is very difficult [1]. Polycrystalline n- and p-type samples of IrSb₃ were prepared by a liquid-solid phase sintering process. The samples were characterized by microprobe analysis, density and X-ray measurements. A variety of electrical and thermal measurements were also performed at high temperatures. The results of the measurements are presented and the potential of this compound as a thermoelectric material is discussed.

EXPERIMENTAL DETAILS

Polycrystalline samples of IrSb₃ were prepared by a liquid-solid phase sintering process. Iridium powder (99.95%) and antimony shots (99.9999%) were loaded in a quartz ampoule about 6 mm in diameter. The ampoule was coated with carbon in order to prevent any interaction of the materials with the quartz and the formation of

oxides at elevated temperatures. The iridium powder was loaded first in the ampoule and the antimony shots were loaded on the top of it. Doping studies were also conducted with platinum and iodine. Platinum powder was mixed together with iridium powder and iodine was introduced in the form of the compound SbI₃. The ampoule was then sealed under vacuum, held vertical in a furnace and heated. Several reaction time durations and temperatures were tried and the best results were obtained for a reaction time of 24 hrs at a temperature of 950 °C. Under these conditions, the samples were the most dense. After reaction, samples about 6 mm in diameter and 10 mm long were easily removed from the ampoules and cut into slices.

Some samples were ground for X-ray diffractometry (XRD) analysis which showed that the samples were single phase. The density of the samples was measured by the immersion technique using toluene as the liquid. The measured densities were found to be between 85 and 95 % of the theoretical density (9.32 g.cm⁻³). Selected samples were polished and their micro structure was investigated under an optical microscope. Microprobe analysis (MPA) was also performed on the samples to check their composition and it was found that most of the samples were slightly antimony-rich (about 76 at. % antimony) but single phase.

Samples about 2 mm thick and 6 mm in diameter were characterized at room temperature by Hall effect and Seebeck coefficient measurements. High temperature Seebeck coefficient, electrical resistivity, thermal conductivity and Hall effect measurements were also performed on selected samples.

RESULTS AND DISCUSSION

Thermoelectric Properties of IrSb₃

Room temperature van der Pauw, Hall coefficient and Seebeck coefficient measurements are summarized in Table 1. The results show that IrSb₃ is a semiconductor. As prepared samples show p-type conductivity while doping with platinum concentration between 0.05 and 0.15 at. % changed the conductivity to n-type. MPA of samples doped with platinum concentrations higher than 0.15 at. % always showed some secondary phases and the volatility limit of platinum in IrSb₃ is about 0.15 at. %. As expected, iodine was found to be a p-type dopant for IrSb₃. The properties of IrSb₃ are qualitatively similar to the results obtained for the isostructural compound CoSb₃ [4]. High p-type carrier mobilities were measured and a maximum of 1380 cm².V⁻¹.s⁻¹ was measured on a sample with a carrier concentration of 7.1 x 10¹⁸ cm⁻³. For lower carrier

concentration, the Hall mobility decreases which is not consistent with the large bandgap of IrSb₃ and the absence of minority carrier compensation effects. Figure 1 shows the Hall mobility values as a function of the Hall carrier concentration for the skutterudite compounds IrSb₃ and CoSb₃ and also state-of-the-art semiconductors Si, Ge and III-V's. Skutterudite compounds have higher hole mobilities than the state-of-the-art semiconductors. These high mobilities are consistent with the predominantly covalent bonds in the skutterudite structure and also to the fact that the valence band is essentially derived from pnictogen-pnictogen bonds in these materials [5].

Table 1. Room temperature properties of n- and p-type IrSb₃ samples.

Sample #	Nominal dopant (at.%)	Conductivity type	ρ	n/p	μ_H	α
2NA11	0.21	p	0.19	6.33	532	30
4NA77	-	p	0.43	1.54	947	62
2IS72	-	p	0.52	1.12	1076	77
1NA76	-	p	0.64	0.71	1380	94
2IS50	0.15 Pt	n	8.36	3.3	24	120
2IS32	0.13 Pt	n	14.39	1.29	34	275
4IS32	0.1 Pt	n	70.3	0.126	72	302
1IS35	0.05 Pt	n	854	0.072	10	345

Electrical resistivity ρ (m Ω .cm), Hall carrier concentration n/p ($\times 10^{19}$.cm⁻³), Hall mobility μ_H (cm².V⁻¹.s⁻¹), Seebeck coefficient α (μ V.K⁻¹).

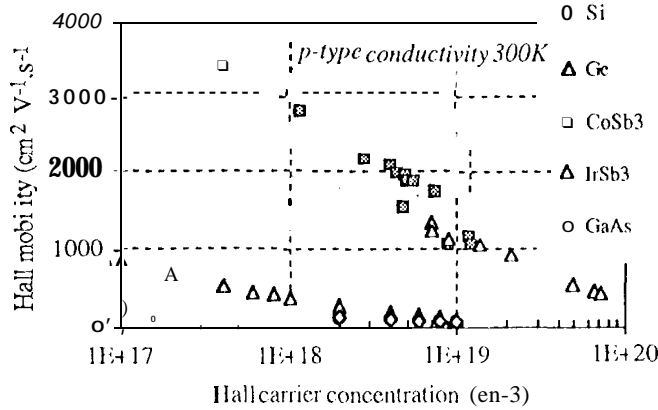


Figure 1: Room temperature hall mobility for p-type IrSb₃ and CoSb₃ as a function of Hall carrier concentration. Values for p-type Si, Ge and GaAs are also shown for comparison.

N-type samples have higher electrical resistivity than p-type samples because n-type Hall mobilities are substantially lower than p-type. N-type Seebeck coefficients are larger than p-type Seebeck coefficients which indicates, as for CoSb₃ [4], a difference in the hole and electron effective masses. An estimation of the effective masses can be made from the room temperature values of the hall carrier concentration and Seebeck coefficient as follows. The Seebeck coefficient (α) can be expressed using generalized Fermi-Dirac statistics formalism and assuming acoustic phonon scattering of the charge carriers:

$$\alpha = \pm \frac{k}{e} \left(2 \frac{F_1(\xi)}{F_0(\xi)} - \xi \right) \quad (1)$$

where k is the Boltzmann constant, e the electron charge, ξ the Fermi

level, and F_1 and F_0 are Fermi integrals. Using the same formalism, the Hall carrier concentration (n/p) can be expressed as:

$$n/p = 4/\sqrt{\pi} (2\pi m^* kT/h^2)^{3/2} F_{1/2}(\xi) \quad (2)$$

Using the room temperature values of the Seebeck coefficient and assuming acoustic phonon scattering, the Fermi level ξ can be calculated from equation (1) and used in equation (2) to calculate the effective mass m^* . Using the data tabulated in table 1, an average mass of 0.17 and 1.51 m_0 was calculated for the holes and the electrons, respectively.

Figure 2 shows the electrical resistivity values as a function of the temperature for several n and p-type IrSb₃ samples with different doping levels. N-type samples have higher resistivity values than p-type samples which do not show any intrinsic behavior in the investigated range of temperature. N-type samples clearly show an intrinsic behavior at high temperatures and a bandgap of 1.18 eV was estimated from the linear variations of the electrical resistivity at high temperatures.

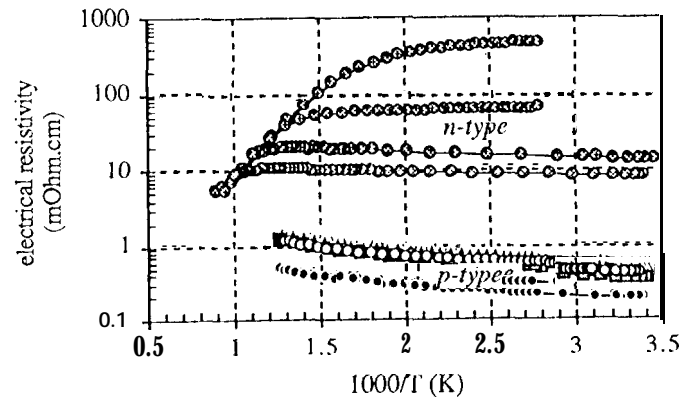


Figure 2: Electrical resistivity as a function of temperature for p- and n-type IrSb₃.

The variations of the Hall mobility as a function of temperature are shown in Figure 3. The Hall mobility of p-type samples decreases only slowly with temperature and a maximum value of 600 cm².V⁻¹.s⁻¹ was measured at 500 °C. The Hall mobility of n-type samples is negative up to about 300 °C and becomes positive for higher temperatures, increasing up to about 700 °C. This is due to compensation effects by high hole mobility holes. The high temperature Seebeck coefficient values of n- and p-type IrSb₃ samples are shown in Figure 4. The p-type Seebeck coefficients increase up to a temperature of about 650 °C, reaching a maximum value of about 200 μ V.K⁻¹, and then decreases. For lightly doped n-type samples, minority carrier compensation effects are also observed and the Seebeck coefficient changes sign at relatively low temperature, becomes positive and then follows the variations of typical p-type samples at high temperatures. For n-type samples with a high doping level, the Seebeck coefficient remains n-type up to a temperature of 700 °C.

The thermal conductivity of two n-type and one p-type IrSb₃ samples was calculated from thermal diffusivity and heat capacity measurements up to 700 °C and the results are shown in Figure 5. The thermal conductivity decreases from a room temperature of about 10.5 W.m⁻¹.K⁻¹ to a minimum value of about 3.4 W.m⁻¹.K⁻¹ at 700 °C for the p-type sample. An estimate of the lattice thermal

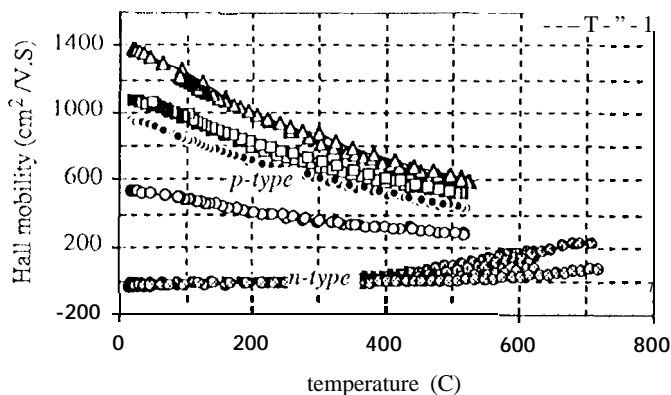


Figure 3: Hall mobility as a function of temperature for p- and n-type IrSb₃.

conductivity of IrSb₃ can be made by calculating the electronic contribution to the total thermal conductivity using the Wiedemann-Franz law, the value of the Lorenz number being calculated using the Fermi level value obtained from equation (1). The lattice thermal conductivity (λ_{ph}) was estimated at 9.5 W.m⁻¹.K⁻¹ and is clearly the dominant contribution.

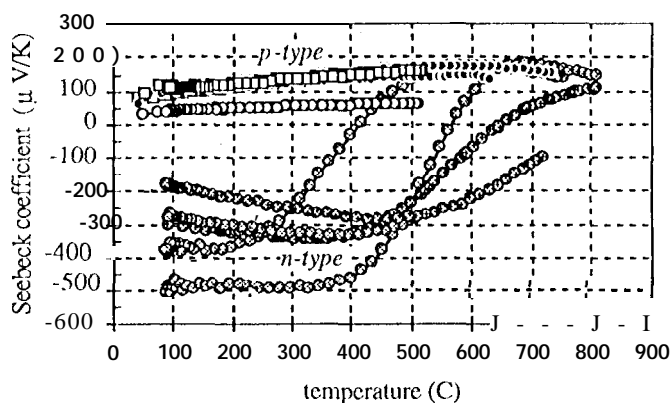


Figure 4: Seebeck coefficient as a function of temperature for p- and n-type CoSb₃.

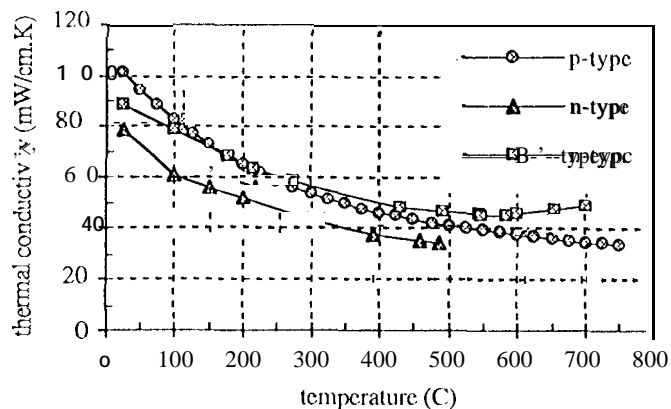


Figure 5: Thermal conductivity as a function of temperature for p- and n-type CoSb₃.

Figure 6 shows the calculated ZT values for two p-type samples and two n-type samples as a function of temperature. A maximum ZT value of 0.4 was achieved at about 550°C for p-type IrSb₃. This value is in agreement with the maximum value predicted from

transport properties modeling of IrSb₃ [10]. ZT values are increasing with temperature, suggesting that higher values might be obtained at higher temperature. However, although the decomposition temperature of IrSb₃ is 1141°C, partial decomposition of the samples can occur in dynamic vacuum above 600 °C and use of this material above this temperature would be difficult. For the n-type samples, ZT values are increasing with temperature, reaching a maximum of about 0.15 at a temperature of about 500 °C and then decrease with increasing temperature corresponding to the decrease of the Seebeck coefficient above this temperature for heavily doped n-type samples.

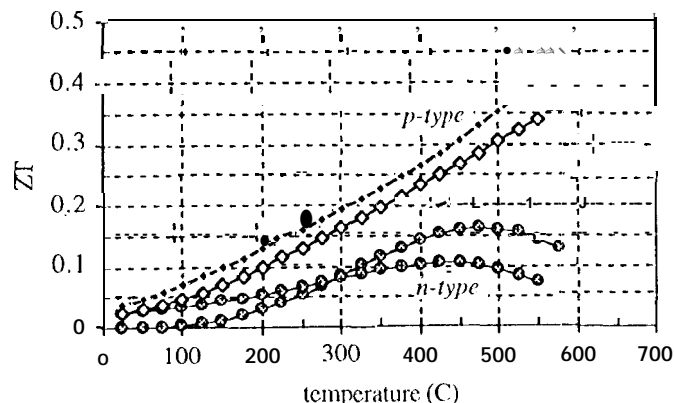


Figure 6: ZT values as a function of temperature for some p- and n-type IrSb₃ samples.

Conventional theory for a single band semiconductor indicates that the optimum thermoelectric figure of merit depends on the scattering mechanism and a material parameter $\beta = m^{*3/2} \mu / \lambda_{ph}$ where m^* is the carrier effective mass, μ is the carrier mobility in cm².V⁻¹.s⁻¹ and λ_{ph} is the lattice thermal conductivity in mW.cm⁻¹.K⁻¹. β can be calculated from the estimated electron and hole masses, the estimated lattice thermal conductivity of 10.3 W.m⁻¹.K⁻¹ and the measured values of the Hall mobilities for the holes and electrons. The Hall mobilities were extrapolated at a carrier concentration of 10¹⁸ cm⁻³ for n- and p-type IrSb₃ using the variations of the Hall mobility as a function of carrier concentration determined in this study. The values of β for n and p-type IrSb₃ are compared to p-type SiGe and FeSi₂ in Table 2.

Table 2. Some properties of n- and p-type IrSb₃.

	m^*/m_0	μ (cm ² .V ⁻¹ .s ⁻¹)	λ_{ph} (mW.cm ⁻¹ .K ⁻¹)	β
p-type	0.17	1800	95	1.33
n-type	1.51	100	95	1.95
p-FeSi ₂	4 *	4 *	40 *	0.8 *
p-SiGe	1 *	40 *	44 *	0.9 *

* [6]

Although the maximum achievable ZT depends on several additional parameters not included in β , the results show that IrSb₃ is an interesting material with a good thermoelectric potential. However, relatively low ZT values were obtained mainly because the lattice thermal conductivity of IrSb₃ is too large. The results also show that n-type samples might have higher ZT values than p-type material despite the exceptionally high Hall mobilities of p-type samples.

High Temperature Heat-Treatment

High-temperature heat-treatments were also conducted in dynamic vacuum to attempt controlling the doping level of the samples by changing their stoichiometry. The impact of the high-temperature heat-treatments on the properties of IrSb_3 samples prepared by liquid-solid phase sintering was investigated. Several duration times and temperatures were tried. It was found by MPA and XRD that the samples partially decomposed during the heat-treatment and an IrSb_2 layer developed on the surface of the samples during the heat-treatments. The thickness of this layer depends on the heat-treatment conditions and the quality of the samples. For a typical heat-treatment at a temperature 950°C for about 20 minutes on a sample about 1 mm thick, an IrSb_2 layer of about 50 \AA developed.

Heat-treating the samples at a temperature of 950°C for about 2.0 minutes substantially increased the Seebeck coefficient of the samples. The influence of the $\text{IrSb}_3/\text{IrSb}_2$ interface on the properties of heat-treated IrSb_3 samples was investigated and it was found that this increase in the Seebeck coefficient was associated to the $\text{IrSb}_3/\text{IrSb}_2$ interface. Indeed, the increase in the Seebeck coefficient could no longer be observed when the IrSb_2 layer was removed. Measuring the resistivity of these samples by the van der Pauw technique led to low resistivity values (slightly increased compared to non heat-treated samples) which, combined with the increase in Seebeck coefficient values, led to high ZT values reported in [7]. However, this technique is not suitable to measure the resistivity of a two layer sample. We attempted to measure the resistivity of the samples by various bonding, brazing or pressing contacts techniques. None of these techniques was successful because of the difficulties to find an adequate bonding material without altering significantly the surface of the samples and we could not find a technique to reliably measure the resistivity of these heat-treated samples.

CONCLUSION

High ZT values might be possible for materials with the skutterudite structure if one can find a skutterudite material with a substantially lower thermal conductivity, retaining the good basic properties of IrSb_3 , such as high carrier mobility. Reduction of the thermal conductivity can be achieved, for example, by increasing phonon scattering by alloying with isostructural compounds [8] or developing ternary or even quaternary skutterudite related phases [9]. Considering the large number of materials having the skutterudite structure [9] and the possibilities of tailoring composition and bandgap in these materials, one should be able to find a material with a good potential for high ZT values.

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